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PROGRESS IN ACETYLENE CHEMISTRY

In an article (1) on the chemistry of acetylene and its derivatives which appeared in Vestnik Akademii Nauk SSSR, No 11, 1949, the author stated that extensive studies in this field have been carried on for a number of years in a laboratory supervised by I. N. Nazarov, Corresponding Member, Academy of Sciences USSR. In his laboratory, a unit of the Institute of Organic Chemistry, Academy of Sciences USSR, a simple method was developed 10 years ago for synthesizing various vinylacetylene alcohols (vinylethinylcarbinols).

Vinylethinylcarbinols are easily polymerized into a solid vitreous mass and can be used as a reliable adhesive for firmly gluing metals, glass, porcelain, marble, minerals, plastics, and other materials. These carbinols were quickly adopted for actual use and have proved themselves of value in the optical, instrument and tool, marble, automobile repair, public utilities, and other branches of USSR industry, particularly during World War II.

Systematic research on vinylethinylcarbinols instituted in this laboratory has revealed the unusual richness and variety of synthetics. Of the many new reactions discovered by Nazarov and his colleagues, the one for the hydration and cyclization of divinylacetylene hydrocarbons into cyclopentenones is most significant since it permits the development of a very simple method for the conversion of acetylene into compounds of the cyclopentane series which are difficult to synthesize. These compounds are found in petroleum and other important natural products.

Recent examples of this phase of acetylene chemistry are afforded by two investigations, resumes of which follow:

In the first investigation (2), Nazarov and S. S. Bakhmutskaya began by hydrating 1, 2-bis(1' - cyclohexenyl) acetylene in an aqueous solution of methanol in the presence of sulfuric acid and $HgSO_4$ and obtained good yields of 1-hexenyl 1-hexenylmethyl ketone which was hydrogenated with a Pt catalyst to form cyclohexyl cyclohexylmethyl ketone. The cyclization of 1-hexenyl -1 hexenylmethyl ketone with H_3PO_4 gave spiro /cyclohexane-1, 1'-indan-3-one/, and the condensation of vinylacetylene with cyclohexl cyclohexylmethyl ketone gave good yields of 1, 2-dicyclohexyl-5-hexen-3-yn-2-ol which was hydrogenated with Pt catalyst to 1, 2-dicyclohexyl-2-hexanol and dehydrated to 1, 2-dicyclohexyl-1,5-hexadien-3-yne. The latter compound was hydrogenated to 1, 2-dicyclohexylhexane

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and was also hydrated in an aqueous methanol solution to 1,3-dicyclohexyl-1,5-hexadiene-3-one which was easily cyclized with H_3PO_4 to 1,2-dicyclohexyl-3-methyl-1-cyclopenten-5-one.

A similar procedure was carried out in the second investigation (3) in which Nazarov collaborated with L. N. Pinkina: who showed that upon condensation of isobutyrone with vinylacetylele, 5-isopropyl-6-methyl-1-hepten-3-yn-5-ol was formed with good yields. Then this compound was easily dehydrated.by dilute sulfuric acid to 5-isopropyl-6-methyl-1,5-heptadien-3-yne. Upon heating this latter substance in aqueous methanol with H_2SO_4 and $HgSO_4$, 5-isopropyl-6-methyl-1,5-heptadien-4-one was formed which, under the action of acid (phosphoric sulfuric, hydrochloric, and p-tolenesulfonic acids), was transformed into 2-isopropyl-3,3,4-trimethyl-4-cyclopenten-1-one.

The Vestnik Akademii Nauk SSSR article (1) also notes another very interesting phase of acetylene chemistry dealing with the synthesis of heterocyclic compounds of the pyran, thiopyran, and piperidine series which form the basis for many natural and synthetic medicinal preparations and physiologically active substances.

Three current studies on such compounds are available. In one of these, Nazarov and I. V. Torgov (4) began with the condensation of 2,2-dimethyltetrahydro-1,4-pyrone with acetylene in the presence of powdered KOH giving 30 percent 2,2-dimethyl-4-ethynyltetrahydro-4-pyranol, which during partial hydrogenation with a Pd catalyst was transformed into the corresponding vinyltetrahydropyranol. This latter compound upon dehydration with p-toluene sulfonic acid then gave 68 percent 2,2-dimethyl-4-vinyl-3,6-dihydropyran which easily condensed with maleic anhydride forming the normal additional product. At 160-185 degrees centigrade, 2,2-dimethyl-4-vinyl-3,6-dihydropyran condensed easily with 1,3-dimethyl-1-cyclopenten-5-one with the formation of a tricyclic ketone of the pyran series containing a cyclopentanone nucleus with an angular methyl group. The oxidation of 1,3-dimethyl-1-cyclopenten-5-one with SeO in a glacial acetic acid solution gave 1,3-dimethyl-1-cyclopenten-4,5-dione which condensed with 2,2-dimethyl-4-vinyl-3,6-dihyropyran forming a tricyclic diketone.

Three colleagues, V. Ya. Raygorodskaya, F. I. Gotman, and V. A. Rudenko, worked with Nazarov in another research effort (5) on heterocyclic compounds. They first reacted ethylamine and ethanolamine with allyl isopropenyl ketone and its methoxy derivatives (obtained by the addition of CH_3OH across one or both double bonds) to obtain 1-ethyl-2,5-dimethyl-4-piperidone and 1-(beta-hydroxyethyl)-2,5-dimethyl-4-piperidone in good yields. The latter compound did not react with acetylene, vinylacetylene, or Grignard reagents, but the former compound condensed with acetylene to give 85 percent 1-ethyl-2,5-dimethyl-4-ethynyl-4-piperidol which was then selectively hydrogenated with a Pd catalyst to 1-ethyl-2,5-dimethyl-4-vinyl-4-piperidol, and was exhaustively hydrogenated to give 1,4-diethyl-2,5-dimethyl-4-piperidol. The 1-(beta-hydroxyethyl)-2,5-dimethyl-4-piperidone readily gave the crystalline 2,4-dinitro-phenyl-hydrazone but was catalytically hydrogenated with a Ni catalyst to 1-(beta-hydroxyethyl)-2,5-dimethyl-4-piperidol.

1,2,5-trimethyl-4-piperidols were synthesized by Nazarov, Raygorodskaya, and Rudenko (6) as follows: The condensation of 1,2,5-trimethyl-4-piperidone with acetylene in the presence of powdered KOH gave 80 percent 1,2,5-trimethyl-4-ethynyl-4-piperidol which was isolated in the form of two stereoisomers. Both isomers, upon heating with powdered KOH, decomposed into acetylene and the initial piperidone. Selective hydrogenation of the piperidol gave the vinylpiperidol, and exhaustive hydrogenation gave the ethylpiperidol. The condensation of the original piperidone with vinylacetylene produced good yields of 1,2,5-trimethyl-4-vinylethynyl-4-piperidol. Phenyllithium reacted with the original piperidone to yield 1,2,5-trimethyl-4-piperidol. The esters (acetates, propionates, and benzoates) of the piperidyl alcohols were prepared and found to possess physicological (particularly anesthetic) properties.

The latter work of Nazarov (1) and his collaborators with steroid compounds is also of very great importance, for these constitute the basis for the synthesis of animal and plant sterols, steroid hormones, bile acids, antirachitic vitamin D, cardiac aglucones, and other biologically active compounds which play important roles in the activity of animal and plant organisms. It has required almost 100 years to define the structures of these steroid compounds, and the efforts of foreign chemists to synthesize them on the basis of carbon skeletons have not led to positive results.

Nazarov and his fellow-workers, however, developed a very simple and elegant method for the complete synthesis of steroid skeletons, opening up wide horizons for further advances in this field.

The investigation by Nazarov and Torgov (4) form a good example of work in the field of steroids, in view of the fact that tricyclic ketones, similar to cyclo-penta-phenanthrenones, have been synthesized and the introduction of the angular methyl group is dealt with.

In the last 10 years, Nazarov's group has prepared over 1,000 new substances on the basis of acetylene -- substances falling into all classes and subdivisions of organic compounds (1).

For many years, large quantities of acetic acid, rubber, plastics, synthetic fibers, adhesive and impregnating substances, solvents, and numerous other chemical products have been manufactured on the basis of acetylene. In fact, acetylene is one of the basic starting materials in contemporary industrial synthesis. The trend, which was started by Nazarov's school, makes acetylene a promising material for the synthesis of such complicated and important fine organic compounds as the steroids, alkaloids, and substances related to them.

Recently, another series of articles in the field of acetylene chemistry have been initiated by the Chair on the Structure of Organic Compounds of the Order of Lenin State University imeni A. A. Zhdanov in Leningrad. In the first article of the series (7), I. A. Favorskaya described the preparation of the unsaturated ketone, 4,4'-dimethyl-3-methenepentanone-2, by the hydration of beta-tertiary-butylvinylacetylene, as well as a method for preparing beta-tertiary-butylvinylacetylenecarbonic acid and beta-tertiary-butylvinylacetylenecarbonate.

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